



TITLE:

Studies on the Velocity of Copolymerization. (II) : On the Phenomena that the Copolymerization Stops at Very Low Conversions

AUTHOR(S):

Okamura, Seizo; Yamashita, Takao; Tsuchiya, Masako

CITATION:

Okamura, Seizo ...[et al]. Studies on the Velocity of Copolymerization. (II) : On the Phenomena that the Copolymerization Stops at Very Low Conversions. 京都大学化学研究所報告 1950, 23: 75-76

ISSUE DATE:

1950-12-30

URL:

<http://hdl.handle.net/2433/74175>

RIGHT:

$$\frac{dx}{dt} = K_1[G] (A_2 - x_2)^2 e^{-ax/RT}, \quad a = \text{const} \times E, \quad [G] = \text{conc. of gas}$$

In this equation x in the exponential term should be rationally written as $f(x)$ instead of ax , but from the observed data of a differential adsorption heat it might be considered not so remote from the linear function of x . The equation can be integrated as,

$$K_1[G]t = ae^{aA_2} \left\{ \frac{e^{-a(A_2-x_2)}}{a(A_2-x_2)} - \frac{e^{-aA_2}}{aA_2} + \log \frac{A_2-x_2}{A_2} \right. \\ \left. + ax_2 + \frac{a^2(A_2-x_2)^2 - A_2^2}{2 \cdot 2!} + \dots + (-1)^n \frac{a^n(A_2-x_2)^n - A_2^n}{n \cdot n!} + \dots \right\},$$

where

$$a = \alpha/RT$$

But it is not easy to verify this formula directly by the numerical data. So we plot the logarithm to show the relationship between the apparent absorbed volume and the rate constants calculated from the equation which was derived from the foregoing report (*ibid*). If the linear relationship between these two properties is admitted, we can approximately conclude the existence of repulsive interactions among adsorbed particles. The results for the iron-kieselgur catalyst show that this relation holds stepwise, i. e. the plot comes out in such a way as several straight lines with equal inclination and unequal intercepts are connected by curved parts. And the inclinations of the straight parts are scarcely influenced by the variation of temperature. This reason may be interpreted in various ways, but what we can conclude from those results are the existence of repulsions and that activation energy changes with the increase of adsorbed fraction of the surface.

68. Studies on the Velocity of Copolymerization. (II)

On the Phenomena that the Copolymerization Stops at Very Low Conversions.

Seizo Okamura, Takao Yamashita and Masako Tsuchiya.

(Sakurada Laboratory)

The purpose of this report is to give the kinetical explanation on the phenomena that copolymerization stops at very low conversions, in the case copolymerization occurs with comonomers where some of them easily and the others hardly polymerize.

In the theoretical studies of Prof. Sakurada and others (cf. "KOJUGOHANNO" p. 29, 1944 or J. Alfrey et al. J. Chem. Phys., 12 205, 321, 1944 etc.), the following relationship was proved.

$$\frac{dx}{dy} = \frac{1 - \gamma_x \frac{x}{y}}{1 - \gamma_y \frac{x}{y}} \quad \dots\dots\dots (1)$$

in which γ was the monomer reactivity ratio. And in the case that x assigns the mol concentration of easily-polymerizable monomer and y that of hardly-polymerizable one, we obtain

$$\gamma_y \neq 0$$

Therefore, from (1)

$$\frac{dx}{dy} = 1 - \gamma_x \frac{x}{y} \quad \dots\dots\dots (2)$$

Let

$$\frac{x}{y} = z \quad \dots\dots\dots (3)$$

then

$$\frac{dx}{dy} = z + \frac{y}{dy} dz \quad \dots\dots\dots (4)$$

From (2) and (4),

$$z + \frac{y}{dy} dz = 1 - \gamma_x \cdot z$$

then

$$\frac{dy}{y} = \frac{dz}{(\gamma_x - 1)z} \quad \dots\dots\dots (5)$$

By integrating (5)

$$\frac{y}{y_0} = \left\{ \frac{1 + (\gamma_x - 1)z}{1 + (\gamma_x - 1)z_0} \right\}^{\frac{1}{(\gamma_x - 1)}} \quad \dots\dots\dots (6)$$

in which y_0 and z_0 are the initial values respectively. The yield of polymerization p (in mol fraction) is given by the following equation.

$$P = 1 - (x + y) = 1 - (1 + z)y_0 \left\{ \frac{1 - (\gamma_x - 1)z}{1 - (\gamma_x - 1)z_0} \right\}^{\frac{1}{(\gamma_x - 1)}} \quad \dots\dots\dots (7)$$

In the case of copolymerization of acrylonitrile (x) and vinyl-acetate (y), Prof Sakurada obtained followings; (Okamura and Ota, Chem. of High Polymers, Japan, 3, 19, 1946),

$$\gamma_x = 3.2 \quad \gamma_y \neq 0 \quad \dots\dots\dots (8)$$

As shown in the Table 1, calculated by the (7) and (8), pretty satisfactory coincidence between the theory and experimental results was obtained.

Table. 1.

Exp. No.	x_0 (in mole)	z_0 (in weight ratio)	Polym. Time (Mins.)	The Yield of copolym. (p in wt %) when copolymerization stops.	
				obs. value	calculat. value (at z_0)
1	0.7	0.602/0.398	390	80.5	79.5
2	0.5	0.382/0.617	390	58.0	58.3
3	0.3	0.212/0.788	180	27.5	36.0
4	0.2	0.127/0.873	360	28.2	23.0
5	0.1	0.065/0.935	360	13.9	12.5